Claims

1. A method for the surface treatment of a substrate comprising

(i) spreading a layer of hardenable paste over a surface area of the substrate to be treated, the paste comprising at least first and second populations of particles co-dispersed in a water-containing phase, the second population being sufficiently small to pack the interstices between particles of the first population with which it is co-dispersed, at least one of the first and second populations being of reactive binder particles,

(ii) covering a surface area of the paste layer with (a) a flexible membrane or (b) a plate or (c) first a flexible membrane then superimposed thereon a plate, the plate or membrane having an upper-surface and a smooth under-surface, such that in cases (a) and (c) the smooth membrane under-surface, and in case (b) the smooth plate under-surface, is in intimate contact with and conforms to the contours of that surface area of the paste layer, thereby providing a membrane-covered or plate-covered area of the paste layer,

(iii) optionally vibrating the membrane-covered or plate-covered area of the paste layer, such that vibration is transmitted through the membrane or plate, to the paste layer, and

(iv) either removing the membrane, plate or plate and membrane then hardening the paste layer on the substrate, or at least partially hardening the paste layer on the substrate with the membrane, plate or plate and membrane in place.

2. A method as claimed in claim 1 wherein the substrate is a wall, floor, ceiling, column, door, or a section of any of the foregoing.

3. A method as claimed in claim 1 wherein the substrate is a hardened or partially hardened clay, ceramic or cementitious article, or a hardenable,

water-containing clay, ceramic or cementitious mass shaped in the form of the article.

4. A method as claimed in claim 3 wherein the article is, or the mass is shaped in the form of, a roofing tile, a wall tile, a floor tile, a roofing panel, a pipe, a work-top, a paving block or a wall cladding panel

5. A method as claimed in any of claims 1 to 4 wherein the substrate is orientated generally horizontally during step (I) and/or (ii).

6. A method as claimed in any of claims 1 to 4 wherein the substrate is orientated generally vertically during step (I) and/or (ii).

7. A method as claimed in any of the preceding claims wherein in step (i) one or more portions of paste is/are positioned on the substrate and spread as the desired layer by causing the membrane or plate to be pressed into contact with the portion(s) during the covering step (ii), thereby causing the portion(s) to spread as the desired paste layer between the under-surface of the membrane or plate and the article or shaped mass.

8. A method as claimed in any of claims 1 to 6 wherein the membrane or plate is pressed into intimate contact with the paste layer by rolling pressure applied to the membrane or plate or by reduced atmospheric pressure between the membrane or plate and the paste layer.

9. A method as claimed in any of the preceding claims wherein the surface of the substrate is treated prior to spreading the paste layer, to improve binding between it and the paste layer.

10. A method as claimed in any of the preceding claims wherein the flexible membrane is of plastics or paper-based material or the plate is of plastics material or metal.

11. A method as claimed in any of the preceding claims wherein the first particle population of the paste has a weight average particle size in the range 1μm to 500μm and the second particle population has a number average particle size from 0.001μm to 40μm.

12. A method as claimed in claim 6 wherein the first particle population is of reactive binder particles, e.g. cement, and/or fly ash and/or blastfurnace slag particles and the second particle population is of binder particles e.g. microsilica, blastfurnace slag powder or fly ash or of non-binder particles e.g. iron oxide.

13. A process as claimed in claim any of the preceding claims wherein in the paste additionally comprises a population of aggregate particles having a weight average particle size in the range 50μm to 500μm, and/or a population of micro-aggregate particles having a weight average particle size in the range 0.01μm to 50μm and/or a population of micro-fibres having a mean length in the range 100μm to 5mm.

14. A method as claimed in any of the preceding claims wherein the paste is degassed or mixed to minimise entrained gas bubbles prior to being spread on the article or shaped mass.

15. A method as claimed in any of the preceding claims wherein the paste layer on the substrate is hardened or partially hardened with the membrane, plate or plate and membrane in place, and then the membrane, plate or plate and membrane is separated from the hardened or partially hardened paste layer.

16. A method as claimed in any of the preceding claims wherein in step (ii) a membrane is contacted with the paste layer, and a vibrational step (iii) is implemented by vibrating the paste layer through the membrane by pressing into intimate contact an area of the membrane-covered area of the paste layer and a membrane-contact surface of a vibratable plate element contoured to

match that of the membrane-covered area of the paste layer, and causing the vibratable plate element to vibrate while maintaining pressure contact between it and the membrane-covered area of the paste layer, such that vibration is transmitted from the vibratable plate element, through the membrane, to the surface of the paste layer.

17. A method as claimed in any of claims 1 to 15 wherein in step (ii) a plate is contacted with the paste layer, or a membrane is contacted with the paste layer and a plate is superimposed thereon, and a vibrational step (iii) is implemented by pressing a vibrating head element into intimate contact with an area of the plate-covered area of the paste layer, and causing the head element to vibrate while maintaining pressure contact between it and the plate-covered area of paste layer, such that vibration is transmitted through the plate element to the paste layer.

18. A method as claimed in claim 16 or claim 17 wherein the plate is vibrated by contacting a vibrating head element with the side of the plate opposite the paste layer, and causing relative movement between the head element and the contacted plate and membrane-covered area of the paste layer, such that the vibrating head element traverses a desired area of that side.

19. A method as claimed in claim 18 wherein the vibratable plate element is rectangular with uniform transverse cross sectional profile, the vibrating head element is contoured to match that profile, and the head is caused to move longitudinally relative to the plate.

20. A method as claimed in any of claims 16 to 19 wherein the axis or main axis of vibration of the surface of the paste layer of the substrate is generally perpendicular to that surface.

21. A method as claimed in any of claims 16 to 20 wherein vibration of a frequency of at least 10 Hz is transmitted to the surface of the substrate.

22. A process as claimed in any of claims 16 to 21 wherein the frequency and amplitude of the vibration and the duration of the vibration are selected to increase the surface density of paste layer, relative to its density prior to vibration, to a depth of at least 10% of its thickness.

23. A process as claimed in any of claims 16 to 21 wherein the frequency and amplitude of the vibration and the duration of the vibration are selected to increase the surface density of the paste layer, relative to its density prior to vibration, to a depth of at least 25% of its thickness.

24. A process as claimed in any of claims 16 to 21 wherein the frequency and amplitude of the vibration and the duration of the vibration are selected to increase the surface density of the paste layer, relative to its density prior to vibration, to a depth of at least 50% of its thickness.

25 A process as claimed in any of claims 16 to 21 wherein the frequency and amplitude of the vibration and the duration of the vibration are selected to increase the density of the paste layer throughout its entire thickness.

26. A process as claimed in any of claims 16 to 25 wherein the vibration transmitted through the plate or plate and/or membrane has a frequency in the range 15 kHz to 50 kHz.

27. A process as claimed in any of claims 16 to 25 wherein the vibration transmitted through the plate or plate and/or membrane has a frequency in the range 15 kHz to 30 kHz.

28. A process as claimed in any of claims 16 to 25 wherein the vibration transmitted through the plate or plate and/or membrane has an amplitude in the range from 1 μm to 3μm.

29. A process as claimed in any of claims 16 to 28 wherein the vibration transmitted through the plate or plate and/or membrane varies in frequency and/or amplitude.

30. A method as claimed in any of claims 16 to 29 wherein a dry, particle-containing composition is applied to the surface of the paste layer prior to its being covered by the membrane.

31 A method as claimed in claim 30 wherein the particles in the particle-containing composition are colour pigment, silicate granules, metal, or polymer particles.

32. A method as claimed in any of the preceding claims wherein a relief-pattern is formed on the paste layer contact surface of the membrane or plate or interposed between the plate and a membrane-covered area of the article, such that when the plate is pressed into contact with the membrane-covered area of the article and/or vibrated the relief pattern impresses the surface of paste layer.

33. A method as claimed in any of claims 1 to 31 wherein a membrane is in contact with the paste layer and a relief-pattern is impressed into the surface of the paste layer by a tool pressing the upper surface of the membrane when in contact with the paste layer.

34. A process as claimed in any of the preceding claims wherein the substrate is cementitious, containing cement particles and microsilica particles as reactive binder particles.

35. A process as claimed in claim 34 wherein the substrate contains sand.

36. A process as claimed in any of the preceding claims wherein the paste layer comprises cement and after step (iv) the surface of the paste layer is acid-washed and/or exposed to a carbon dioxide-rich atmosphere.

37. A method as claimed in any of the preceding claims for production of cementitious tiles for roofing or wall cladding, wherein the substrate is an at least partially hardened tile or hardenable water-containing cementitious mass shaped in the form of a tile, formed by

(a) providing a mouldable, eventually hardenable mass comprising at least water and reactive binder particles, the latter including at least cement particles,

(b) extruding the mass from an extrusion orifice onto conveyor means adapted to carry the extruded mass as a ribbon away from the extrusion orifice, the ribbon having a lower surface in direct or indirect contact with the conveyor means and an upper surface,

(c) cutting the pressed, ribbon across its width into individual tile format and

(d) optionally at least partially hardening the individual tiles.

and wherein the paste layer is spread after steps (a) and (b) or after steps (a) to (c) or after steps (a) to (d).

38. A method as claimed in claim 37 wherein the conveyor means is provided with a plurality of longitudinally closely adjacent pallets or moulds of individual tile dimensions onto which the ribbon is extruded, and the ribbon is cut into individual tiles across its width between adjacent pallets of moulds.

39. A method as claimed in claim 38 wherein the base of a pallet or mould 8on the conveyor belt has a smooth surface to function as a plate in step (ii) or is lined with a smooth surfaced membrane to function as a plate covered membrane in step (ii), paste is deposited on the said smooth base or membrane, and the ribbon is deposited or pressed onto said base or membrane whereby the paste is spread as a layer on the underside of the tile.

40. A method as claimed in any of claims 36 to 38 wherein, the conveyor means divides into a plurality of tracks after the ribbon is cut into individual tiles, tiles queued on the conveyer are successively transported onto separate tracks for the application of individual membrane or plate covers and/or optional vibrational treatment on each tile at individual stations associated with

each track, and the tracks recombine thereafter to reconstitute the queue of tiles for transport to hardening.